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(54) Catalysts and process for producing olefin polymers

Katalysatoren und Verfahren zur Herstellung von Olefinpolymeren

Catalyseurs et procédé de préparation de polymères d'oléfine

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WO-A-91/14713

- DIE MAKROMOLEKULARE CHEMIE, RAPID COMMUNICATIONS vol. 13, May 1992, BASEL pages 277 - 281, XP266808 PELLICHIA 'Polymerization of ethylene and propene in the presence of organometallic compounds of titanium and zirconium activated with tris(pentafluorophenyl)boron' runs 8, 10, 11,13,15,16
- RAPRA ABSTRACTS vol. 14, no. 25, 5 December 1977, N 7705114L BEIKHOL 'Polymerization of ethylene in ethyl chloride over complex catalyst system modified by acids and Lewis bases'

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Description

The present invention relates to a process for producing olefin polymers by use of a polymerization catalyst comprising a metallocene, an organoaluminum compound, and an ionic compound.

The present invention also relates to a process for producing olefin polymers by use of a polymerization catalyst comprising an ionic metallocene and an organoaluminum compound.

The polymerization of ethylene or an α -olefin by a low-pressure Ziegler process is well known in the art. The catalyst therefor is prepared by mixing an organometallic compound or a hydride of an element of the 1A to 3A Group of the Periodic Table with a compound of a transition metal (an element of the 3B to 2B Group of the Periodic Table), and treating the mixture in suspension or solution or in the absence of a diluent or a solvent.

Known special kinds of catalysts active for olefin polymerization include combinations of aluminoxane with a cyclopentadienyl derivative of a metal of the 4B Group, namely titanium, zirconium, and hafnium. Such catalysts are disclosed in the literature "Ziegler-Natta catalyst and polymerization", Academic Press, New York (1979); Adv. Organomet. Chem. 1899 (1980). Such catalysts advantageously exhibit high catalytic activity and are capable of producing stereoregular polyolefins. However, these catalysts have not been used in industrial polymerization, mainly because the aluminoxane cannot readily be synthesized in a reproducible manner and therefore also the catalysts and the polymers cannot be prepared reproducibly.

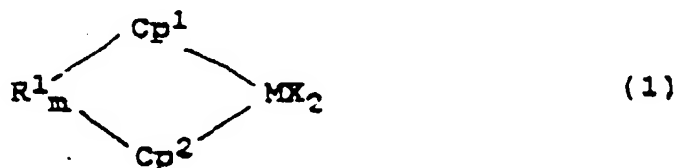
A catalyst which offsets such problems is disclosed in JP-A-3-207704,

which describes a bis(cyclopentadienyl)metal compound prepared by reaction of a metallocene with an ionic compound and the use of the resulting complex as a polymerization catalyst. This catalyst, however, is not satisfactory in the catalyst activity.

Thus, it is an object of the present invention to solve the above problems of the olefin polymerization catalyst employing a metallocene and an organoaluminum compound, and to provide a novel catalyst for polymerization of ethylene or α -olefin.

Another object of the present invention is to provide a process for polymerization of ethylene or α -olefin by use of the above novel catalyst system.

The first object has been achieved by an olefin polymerization catalyst system which comprises a metallocene compound (A), an organoaluminum compound (B), and an ionic compound (C) as catalyst components: the metallocene compound (A) being represented by the general formula (1) below:



where Cp^1 , and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl groups; R^1 is an alkylene group having 1 to 20 carbons, a dialkylsilylene group, a dialkylgermanylene group, an alkylphosphindiy group, or an alkylimino group which crosslink Cp^1 and Cp^2 ; m is 0 or 1; M is titanium, zirconium, or hafnium; and X is fluorine, chlorine bromine, iodine, an alkyl group, or an aryl group; the organoaluminum compound (B) being represented by the general formula (2):



where each of the R^2 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, and at least of one the R^2 groups is an alkyl group; and the ionic compound (C) being represented by the general formula (3) below:



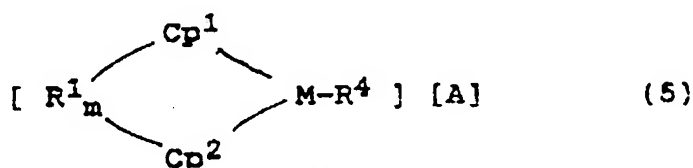
where $[\text{C}]$ is a cation and $[\text{A}]$ is an anion;

the catalyst system further containing a boron compound (D) represented by the general formula (4) below:



where each of the R^3 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the metallocene compound (A).

This object is also achieved by an olefin polymerization catalyst which comprises an ionic metallocene compound (a), and an organoaluminum compound (b) as catalyst components: the ionic metallocene compound (a) being represented by the general formula (5) below:



where Cp^1 , Cp^2 , R^1 , m , and M are the same as defined in the formula (1), R^4 is an alkyl group or an aryl group, and $[A]$ is an anion; and the organoaluminum compound (b) being represented by the general formula (2):



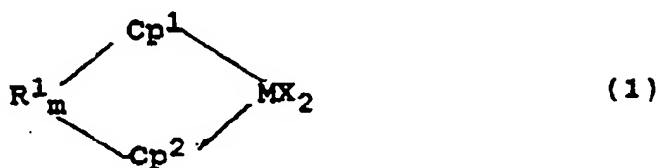
where R^2 is as defined above, and at least one of the R^2 groups is an alkyl group: the catalyst system further containing a boron compound represented by the general formula (4) below:



where R^3 is as defined above; in an amount of from 0.01 mol to 0.8 mol per mol of the ionic metallocene compound (a).

The second object of the present invention is achieved by the provision of a process for the polymerization of ethylene or α -olefin employing the aforementioned catalyst system comprising a metallocene, an organoaluminum compound, an ionic compound, and a boron compound, or a catalyst system comprising an ionic metallocene, an organoaluminum compound, and a boron compound.

The process for producing an olefin polymer, according to an aspect of the present invention, employs a polymerization catalyst system which comprises a metallocene compound (A), an organoaluminum compound (B), and an ionic compound (C) as catalyst components: the metallocene compound (A) being represented by the general formula (1) below:



where Cp^1 , and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl group; R^1 is an alkylene group having 1 to 20 carbons, a dialkylsilylene group, a dialkylgermylene group, an alkylphosphindiy group, or an alkylimino group which crosslink Cp^1 and Cp^2 ; m is 0 or 1; M is titanium, zirconium, or hafnium; and X is fluorine, chlorine, bromine, iodine, an alkyl group, or an aryl group; the organoaluminum compound (B) being represented by the general formula (2):



where each of the R^2 groups is independently a halogen, hydrogen, an alkyl group, alkoxy group, or an aryl group,

and at least of one the R^2 groups is an alkyl group; and the ionic compound (C) being represented by the general formula (3) below:



where [C] is a cation and [A] is an anion;

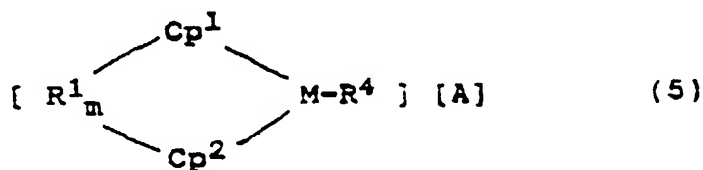
the catalyst system further containing a boron compound (D) represented by the general formula (4) below:



where each of the R^3 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the metallocene compound (A).

The process for producing an olefin polymer, according to another aspect of the present invention, employs an olefin polymerization catalyst which comprises an ionic metallocene compound (a), and an organoaluminum compound (b) as catalyst components:

the ionic metallocene compound (a) being represented by the general formula (5) below:



where Cp^1 , Cp^2 , R^1 , m , and M are the same as defined in the formula (1), R^4 is an alkyl group or an aryl group, and [A] is an anion: and

the organoaluminum compound (b) being represented by the general formula (2):



where R^2 is as defined above, and at least one of the R^2 groups is an alkyl group; the catalyst system further containing a boron compound represented by the general formula (4) below:



where R^3 is as defined above: in an amount of from 0.01 mol to 0.8 mol per mol of the ionic metallocene compound (a).

The metallocene compound (A) used in the present invention is represented by the general formula (1).

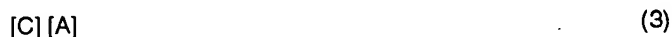
Specific examples thereof include

bis(cyclopentadienyl)titanium dichloride,
 bis(pentamethylcyclopentadienyl)titanium dichloride,
 ethylenebis(indenyl)titanium dichloride,
 ethylenebis(tetrahydroindenyl)titanium dichloride,
 isopropylidene(cyclopentadienyl)(fluorenyl)titanium dichloride,
 dimethylsilylbis(methylcyclopentadienyl)titanium dichloride,
 dimethylsilylbis(2,4-dimethylcyclopentadienyl)titanium dichloride,
 bis(cyclopentadienyl)zirconium dichloride,
 bis(pentamethylcyclopentadienyl)zirconium dichloride, ethylenebis(indenyl)zirconium dichloride,
 ethylenebis(tetrahydroindenyl)zirconium dichloride, isopropylidene(cyclopentadienyl)(fluorenyl)zirconium dichloride,
 dimethylsilylbis(methylcyclopentadienyl)zirconium dichloride,
 dimethylsilylbis(2,4-dimethylcyclopentadienyl)zirconium dichloride,

bis(cyclopentadienyl)hafnium dichloride,
 bis(pentamethylcyclopentadienyl)hafnium dichloride, ethylenebis(indenyl)hafnium dichloride,
 ethylenebis(tetrahydroindenyl)hafnium dichloride,
 isopropylidene(cyclopentadienyl)(fluorenyl)hafnium dichloride,
 5 dimethylsilylbis(methylcyclopentadienyl)hafnium dichloride, dimethylsilylbis(2,4-dimethylcyclopentadienyl)hafnium dichloride.

The ionic metallocene compound (a) employed in the present invention may be prepared, for example, by mixing
 a neutral derivative of a metallocene with an ionic compound (c) in a solvent and, if desired, recovering the product.
 10 The molar ratio of the neutral metallocene derivative to the ionizable ionic compound used therefore is preferably in the range of from 1:0.2 to 1:100, more preferably from 1:1 to 1:10.

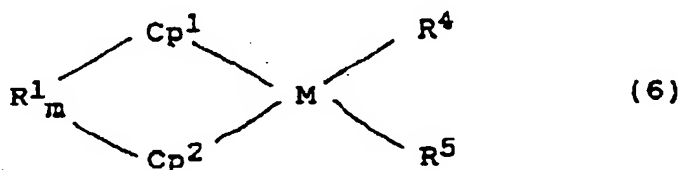
The ionic compound (c) is represented by the general formula (3) below



where [C] is a cation and [A] is an anion.

The solvent used in the above reaction includes toluene, hexane, and methylene chloride, but is not limited thereto.

The neutral metallocene compound used in the preparation of the ionic metallocene compound of the present
 20 invention is represented by the general formula (6) below:



wherein Cp¹, Cp², R¹, m, and M are as defined in the general formula (1) or (5), and R⁵ is hydrogen, a halogen, an
 30 amide group, or an alkyl group.

The specific examples of the neutral metallocene compound include

35 bis(cyclopentadienyl)titaniumdimethyl,
 bis(pentamethylcyclopentadienyl)titaniumdimethyl,
 ethylenebis(indenyl)titaniumdimethyl, ethylenebis(tetrahydroindenyl)titaniumdimethyl,
 isopropylidene(cyclopentadienyl)(fluorenyl)titaniumdimethyl,
 dimethylsilylbis(methylcyclopentadienyl)titaniumdimethyl, dimethylsilylbis(2,4-dimethylcyclopentadienyl)titanium-
 40 dimethyl,
 bis(cyclopentadienyl)zirconiumdimethyl,
 bis(pentamethylcyclopentadienyl)zirconiumdimethyl,
 ethylenebis(indenyl)zirconiumdimethyl,
 ethylenebis(tetrahydroindenyl)zirconiumdimethyl,
 45 isopropylidene(cyclopentadienyl)(fluorenyl)zirconiumdimethyl,
 dimethylsilylbis(methylcyclopentadienyl)zirconiumdimethyl,
 dimethylsilylbis(2,4-dimethylcyclopentadienyl)zirconiumdimethyl,
 bis(cyclopentadienyl)hafniumdimethyl,
 bis(pentamethylcyclopentadienyl)hafniumdimethyl,
 50 ethylenebis(indenyl)hafniumdimethyl,
 ethylenebis(tetrahydroindenyl)hafniumdimethyl,
 isopropylidene(cyclopentadienyl)(fluorenyl)hafniumdimethyl, dimethylsilylbis(methylcyclopentadienyl)hafnium-
 dimethyl, and dimethylsilylbis(2,4-dimethylcyclopentadienyl)hafniumdimethyl.

The organoaluminum compound (B) or (b) is represented by the general formula (2). specific examples thereof
 include trimethylaluminum, triethylaluminum, triisopropylaluminum, tri(n-propyl)aluminum,

triisobutylaluminum, tri(n-butyl)aluminum,

tri(n-hexyl)aluminum, tri(n-octyl)aluminum,
 dimethylaluminum chloride, diethylaluminum chloride,
 diisopropylaluminum chloride, di(n-propyl)aluminum chloride,
 diisobutylaluminum chloride, di(n-butyl)aluminum chloride,
 5 dimethylaluminum ethoxide, diethylaluminum ethoxide,
 diisopropylaluminum ethoxide, di(n-propyl)aluminum ethoxide,
 diisobutylaluminum ethoxide, di(n-butyl)aluminum ethoxide,
 dimethylaluminum hydride, diethylaluminum hydride,
 diisopropylaluminum hydride, di(n-propyl)aluminum hydride,
 10 diisobutylaluminum hydride, and di(n-butyl)aluminum hydride.

The ionic compound (C) or (c) is represented by the general formula (3). It is preferred that the ionic compound readily dissociates. The specific examples thereof include tri(n-butyl)ammonium tetrakis(p-tolyl)borate,

15 tri(n-butyl)ammonium tetrakis(m-tolyl)borate,
 tri(n-butyl)ammonium tetrakis(2,4-dimethylphenyl)borate,
 tri(n-butyl)ammonium tetrakis(3,5-dimethylphenyl)borate,
 tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate,
 N,N-dimethylanilinium tetrakis(p-tolyl)borate,
 20 N,N-dimethylanilinium tetrakis(m-tolyl)borate,
 N,N-dimethylanilinium tetrakis(2,4-dimethylphenyl)borate,
 N,N-dimethylanilinium tetrakis(3,5-dimethylphenyl)borate,
 N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(p-tolyl)borate,
 triphenylcarbenium tetrakis(m-tolyl)borate,
 25 triphenylcarbenium tetrakis(2,4-dimethylphenyl)borate,
 triphenylcarbenium tetrakis(3,5-dimethylphenyl)borate,
 triphenylcarbenium tetrakis(pentafluorophenyl)borate,
 tropylium tetrakis(p-tolyl)borate,
 tropylium tetrakis(m-tolyl)borate.
 30 tropylium tetrakis(2,4-dimethylphenyl)borate,
 tropylium tetrakis(3,5-dimethylphenyl)borate, and
 tropylium tetrakis(pentafluorophenyl)borate.

The boron compound (D) is represented by the general formula (4). The specific examples thereof include trifluoroborane, trichloroborane, tribromoborane, trimethylborane, triethylborane, triisopropylborane, triisobutylborane, tri(n-butyl)borane, triphenylborane, and tri(pentafluorophenyl)borane.

The organoaluminum compound in the present invention is used preferably at a concentration of from 10^{-5} mol/l to 10^{-3} mol/l.

The olefin specifically includes α -olefins such as ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene. Also a mixture of two or more of the olefins may be polymerized. Further, the olefin can be copolymerized with a conjugated or non-conjugated diene such as butadiene, 1,6-hexadiene, 1,4-pentadiene, 1,7-octadiene, 1,8-nonadiene, and 1,9-decadiene; styrene; or a cyclic olefin such as cyclopropene, cyclohexene, norbornene, and dicyclopentadiene.

The polymerization of olefins according to the present invention is conducted by any known process for olefin polymerization with a metallocene compound. The polymerization is conducted, for example, in bulk, in a slurry, or in a gas phase at a temperature of from -80°C to 250°C , preferably from 25°C to 80°C .

In the first aspect of the present invention, the olefin is polymerized, for example, by mixing the metallocene compound (A) and the organoaluminum compound (B) with an olefin, and the ionic compound (C) containing the boron compound (D) is brought into contact with the above mixture. In the olefin polymerization, the molar ratio of the metallocene compound (A) to the ionic compound (C) is normally in the range of from 1:0.2 to 1:100, preferably from 1:1 to 1:10. The boron compound (D) is added in an amount of from 0.01 mol to 0.8 mol, preferably from 0.05 mol to 0.5 mol per mol of the metallocene compound (A). Thereby the activity of the catalyst system is greatly improved. On the contrary, if the boron compound (D) is used in an amount of less than 0.01 mol, or more than 0.8 mol per mol at the metallocene compound (A), the catalyst activity is extremely low.

In the second aspect of the present invention, the olefin is polymerized, for example, by preparing an ionic metallocene compound (a) by mixing a neutral metallocene derivative with an ionic compound in a solvent, adding thereto a boron compound, and bringing the mixture into contact with a mixture of an organoaluminum compound (b) and an olefin. In the olefin polymerization, the boron compound is added in an amount of from 0.01 mol to 0.8 mol, preferably

from 0.05 mol to 0.5 mol per mol of the ionic metallocene compound (a). Thereby the activity of the catalyst system is greatly improved. On the contrary, if the boron compound is used in an amount of less than 0.01 mol, or more than 0,8 mol per mol of the ionic metallocene compound (a), the catalyst activity is extremely low.

The present invention is described in more detail by reference to examples without limiting the invention in any way.

Example 1

In a 2-liter autoclave, 500 ml of toluene was placed. Thereto 0.66 mmol of triethylaluminum was added, and the mixture was stirred for 10 minutes. To this solution, a solution of 1.3 μ mol of ethylenebis(indenyl)zirconium dichloride in 1 ml of toluene was added, and the mixture was stirred for 20 minutes. Then 500 ml of propylene was introduced, and the mixture was stirred for 10 minutes. Further, 1.3 μ mol of N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate and 0.13 μ mol of tris(pentafluorophenyl)borane were pressed into the autoclave with 10 ml of toluene, and polymerization was allowed to proceed at 40°C for one hour. The reaction product was dried in vacuo at about 70°C for 6 hours. Thus 160 g of propylene polymer was obtained.

Comparative Example 1

Polymerization was conducted in the same manner as in Example 1 except that tris(pentafluorophenyl)borane was not added. Thereby 95 g of propylene polymer was obtained.

Comparative Example 2

Polymerization was conducted in the same manner as in Example 1 except that the amount of tris(pentafluorophenyl)borane was changed to 1.3 μ mol. Thereby 21 g of propylene polymer was obtained.

Example 2

In a 2-liter autoclave, 500 ml of toluene was placed. Thereto 0.66 mmol of triethylaluminum was added, and the mixture was stirred for 10 minutes. To this solution, a solution of 5 μ mol of isopropylidene(cyclopentadienyl)(fluorenyl) zirconium dichloride in 1 ml of toluene was added, and the mixture was stirred for 20 minutes. Then 500 ml of propylene was introduced thereto, and the mixture was stirred for 10 minutes. Further, 6.6 μ mol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and 0.66 μ mol of tris(pentafluorophenyl)borane were pressed into the autoclave with 10 ml of toluene, and polymerization was allowed to proceed at 40°C for one hour. The reaction product was dried in vacuo at about 70°C for 6 hours. Thus 95 g of propylene polymer was obtained.

Comparative Example 3

Polymerization was conducted in the same manner as in Example 2 except that tris(pentafluorophenyl)borane was not added. Thereby 20 g of propylene polymer was obtained.

Comparative Example 4

Polymerization was conducted in the same manner as in Example 2 except that the amount of tris(pentafluorophenyl)borane was changed to 6.6 μ mol. Thereby 15 g of propylene polymer was obtained.

Example 3

A solution of 0.66 mmol triethylaluminum in 5 ml of toluene was placed in a 2-liter autoclave as the reactor. The temperature of the reactor was controlled to be at 70°C. Therein, 1.4 liters of propylene was introduced, and the mixture was stirred at a rate of 1200 rpm for 10 minutes.

6.6 μ mol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and 0.66 μ mol of tris(pentafluorophenyl)borane were dissolved in 10 ml of toluene. Separately, 5 μ mol of ethylenebis(indenyl)zirconiumdimethyl was dissolved in 10 ml of toluene. These solutions were mixed and stirred at room temperature for 5 minutes.

The resulting catalyst mixture was charged into the reactor with nitrogen pressure. Thereby the temperature in the reactor rose up to 75°C. At the end of the polymerization reaction, the reactor was cooled, and the unreacted propylene gas discharged from the reactor. The reaction product was dried in vacuo at about 70°C for 6 hours. Thus 695 g of propylene polymer was obtained.

Comparative Example 5

Polymerization was conducted in the same manner as in Example 3 except that tris(pentafluorophenyl)borane was not added. Thereby 116 g of propylene polymer was obtained.

Comparative Example 6

Polymerization was conducted in the same manner as in Example 3 except that the amount of tris(pentafluorophenyl)borane was changed to 6.6 μmol . Thereby 25 g of propylene polymer was obtained.

Example 4

A solution of 0.66 mmol triethylaluminum in 5 ml of toluene was placed in a 2-liter autoclave as the reactor. The temperature of the reactor was controlled to be at 70°C. Therein, 1.4 liters of propylene was introduced, and the mixture was stirred at a rate of 1200 rpm for 10 minutes.

72 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and 7.2 μmol of tris(pentafluorophenyl)borane were dissolved in 10 ml of toluene. Separately, 55 μmol of isopropylidene(cyclopentadienyl)(fluorenyl)zirconiumdimethyl was dissolved in 10 ml of toluene. These solutions were mixed and stirred at room temperature for 5 minutes.

The resulting catalyst mixture was charged into the reactor with nitrogen pressure. Thereby the temperature in the reactor rose up to 75°C. At the end of the polymerization reaction, the reactor was cooled, and the unreacted propylene was discharged from the reactor. The reaction product was dried in vacuo at about 70°C for 6 hours. Thus 410 g of propylene polymer was obtained.

Comparative Example 7

Polymerization was conducted in the same manner as in Example 4 except that tris(pentafluorophenyl)borane was not added. Thereby 90 g of propylene polymer was obtained.

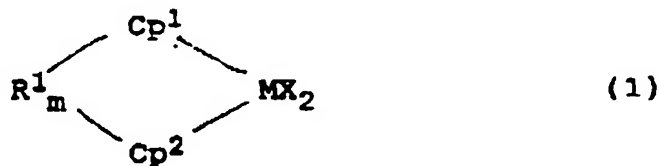
Comparative Example 8

Polymerization was conducted in the same manner as in Example 4 except that the amount of tris(pentafluorophenyl)borane was changed to 72 μmol . Thereby 45 g of propylene polymer was obtained.

As described above, olefin polymers were produced with high efficiency with a high catalyst activity by use of a catalyst comprising a metallocene compound, an organoaluminum compound, and an ionic compound together with a boron compound, or a catalyst comprising an ionic metallocene compound, an organoaluminum compound, and a boron compound.

Claims

1. A process for producing an olefin polymer by use of a polymerization catalyst system, which comprises a metallocene compound (A), an organoaluminum compound (B), and an anionic compound (C) as catalyst components: the metallocene compound (A) being represented by the general formula (1) below:



where Cp^1 , and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl group; R^1 is an alkylene group having 1 to 20 carbons, a dialkylsilylene group, a dialkylgermylene group, an alkylphosphindiy group, or an alkylimino group which crosslink Cp^1 and Cp^2 ; m is 0 or 1; M is titanium, zirconium, or hafnium; and X is fluorine, chlorine, bromine, iodine, an alkyl group, or an aryl group; the organoaluminum compound (B) being represented by the general formula (2):



where each of the R^2 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, and at least one of the R^2 groups is an alkyl group; and the ionic compound (C) being represented by the general formula (3) below:

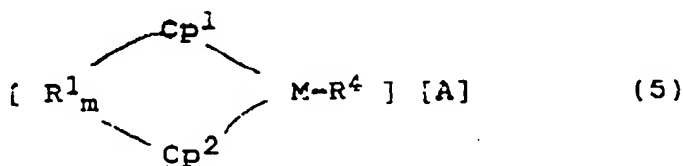


where [C] is a cation and [A] is an anion;
the catalyst system further containing a boron compound (D) represented by the general formula (4) below:



where each of the R^3 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the metallocene compound (A).

2. A process for producing an olefin polymer according to claim 1, wherein the catalyst system contains the boron compound (D) in an amount of from 0.05 mol to 0.5 mol per mol of the metallocene compound (A).
3. A process for producing an olefin polymer according to claim 1 or 2, wherein the metallocene compound (A) and the organoaluminum compound (B) are mixed with the olefin, and the mixture is brought into contact with the ionic compound (C) containing the boron compound (D).
4. A process for producing an olefin polymer by use of a polymerization catalyst system, which comprises an ionic metallocene compound (a), and an organoaluminum compound (b) as catalyst components:
the ionic metallocene compound (a) being represented by the general formula (5) below:



where Cp^1 , and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl group; R^1 is an alkylene group, a dialkylsilylene group, a dialkylgermylene group, an alkylphosphindyl group, or an alkylimino group, R^1 having 1 to 20 carbons and crosslinking Cp^1 and Cp^2 ; m is 0 or 1; R^4 is an alkyl group or an aryl group; M is titanium, zirconium, or hafnium; and [A] is an anion; and the organoaluminum compound (b) being represented by the general formula (2):



where each of the R^2 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, and at least one of the R^2 groups is an alkyl group; the catalyst system further containing a boron compound represented by the general formula (4) below:



where each of the R^3 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the ionic metallocene compound (a).

5. A process for producing an olefin polymer according to claim 4, wherein the catalyst system contains the boron

compound in an amount of from 0.05 mol to 0.5 mol per mol of the ionic metallocene compound (A).

6. A process for producing an olefin polymer according to claim 4 or 5, wherein the ionic metallocene compound (a) is added to the boron compound, and the resulting mixture is brought into contact with the organoaluminum compound and the olefin.
7. A process for producing an olefin polymer according to any of claims 1 to 6, wherein the boron compound is selected from trifluoroborane, trichloroborane, tribromoborane, triphenylborane, and tris(pentafluorophenyl)borane.
8. A process for producing an olefin polymer according to any of claims 1 to 7, wherein the olefin is selected from ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene.
9. A catalyst for polymerization of an olefin, which comprises a metallocene compound (A), an organoaluminum compound (B), and an ionic compound (C) as catalyst components:
the metallocene compound (A) being represented by the general formula (1) below:



where Cp¹, and Cp² are independently a substituted or unsubstituted cyclopentadienyl group; R¹ is an alkylene group having 1 to 20 carbons, a dialkylsilylene group, a dialkylgermylene group, an alkylphosphindiy group, or an alkylimino group which crosslink Cp¹ and Cp²; m is 0 or 1; M is titanium, zirconium, or hafnium; and X is fluorine, chlorine, bromine, iodine, an alkyl group, or an aryl group; the organoaluminum compound (B) being represented by the general formula (2):



where each of the R² groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, and at least of one of the R² groups is an alkyl group; and the ionic compound (C) being represented by the general formula (3) below:



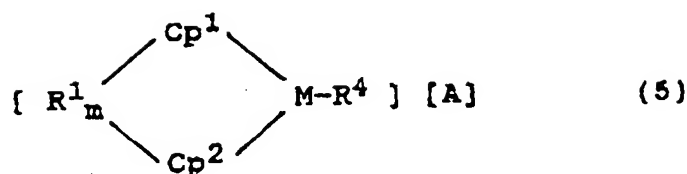
where [C] is a cation and [A] is an anion;

the catalyst system further containing a boron compound (D) represented by the general formula (4) below:



where each of the R³ groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the metallocene compound (A).

10. A catalyst for polymerization of an olefin, which comprises an ionic metallocene compound (a), and an organoaluminum compound (b) as catalyst components:
the ionic metallocene compound (a) being represented by the general formula (5) below:



where Cp^1 , and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl group; R^1 is an alkylene group having 1 to 20 carbons, a dialkylsilylene group, a dialkylgermanylene group, an alkylphosphindiyl group, or an alkylimino group, R^1 crosslinking Cp^1 and Cp^2 ; m is 0 or 1; R^4 is an alkyl group or an aryl group; M is titanium, zirconium, or hafnium; and $[\text{A}]$ is an anion; and the organoaluminum compound (b) being represented by the general formula (2):



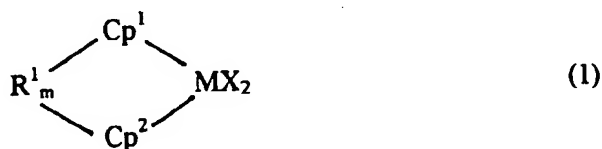
where each of the R^2 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, and at least one of the R^2 group is an alkyl group; the catalyst system further containing a boron compound represented by the general formula (4) below:



where each of the R^3 groups is independently a halogen, hydrogen, an alkyl group, an alkoxy group, or an aryl group, in an amount of from 0.01 mol to 0.8 mol per mol of the ionic metallocene compound (a).

Patentansprüche

- Verfahren zur Herstellung eines Olefinpolymers unter Verwendung eines Katalysatorsystems für die Polymerisation, umfassend eine Metallocenverbindung (A), eine Organoaluminiumverbindung (B) und eine ionische Verbindung (C) als Katalysatorkomponenten, wobei die Metallocenverbindung (A) durch die nachstehende allgemeine Formel (1) wiedergegeben ist:



in der Cp^1 und Cp^2 unabhängig voneinander substituierte oder unsubstituierte Cyclopentadienylgruppen sind; R^1 ein Alkylrest mit 1 bis 20 Kohlenstoffatomen, ein Dialkylsilylen-, Dialkylgermanylen-, Alkylphosphindiyl- oder Alkyliminorest ist, der Cp^1 und Cp^2 verbindet; m 0 oder 1 ist; M ein Titan-, Zirkonium- oder Hafniumatom ist und X ein Fluor-, Chlor-, Brom- oder Iodatome, ein Alkyl- oder Arylrest ist; wobei die Organoaluminiumverbindung (B) durch die allgemeine Formel (2) wiedergegeben ist:



in der jeder der Reste R^2 unabhängig ein Halogen- oder Wasserstoffatom, ein Alkyl-, Alkoxy- oder Arylrest ist und mindestens einer der Reste R^2 ein Alkylrest ist; wobei die ionische Verbindung (C) durch die nachstehende allgemeine Formel (3) wiedergegeben ist:

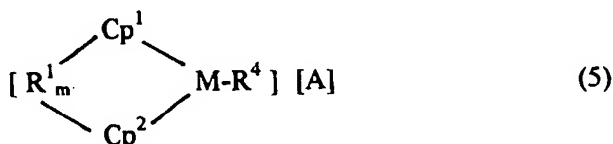


in der [C] ein Kation und [A] ein Anion ist;
wobei das Katalysatorsystem außerdem eine Borverbindung (D) der nachstehenden allgemeinen Formel (4) in einer Menge von 0.01 mol bis 0.8 mol pro mol der Metallocenverbindung (A) enthält:



wobei jeder der Reste R^3 unabhängig ein Halogen- oder Wasserstoffatom, ein Alkyl-, Alkoxy- oder Arylrest ist.

2. Verfahren zur Herstellung eines Olefinpolymers nach Anspruch 1, wobei das Katalysatorsystem die Borverbindung (D) in einer Menge von 0.05 mol bis 0.5 mol pro mol der Metallocenverbindung (A) enthält.
3. Verfahren zur Herstellung eines Olefinpolymers nach Anspruch 1 oder 2, wobei die Metallocenverbindung (A) und die Organoaluminiumverbindung (B) mit dem Olefin gemischt werden und das Gemisch mit der ionischen Verbindung (C), die die Borverbindung (D) enthält, in Kontakt gebracht wird.
4. Verfahren zur Herstellung eines Olefinpolymers unter Verwendung eines Katalysatorsystems für die Polymerisation, umfassend eine ionische Metallocenverbindung (a) und eine Organoaluminiumverbindung (b) als Katalysatorkomponenten,
wobei die ionische Metallocenverbindung (a) durch die nachstehende allgemeine Formel (5) wiedergegeben ist:



in der Cp^1 und Cp^2 unabhängig voneinander substituierte oder unsubstituierte Cyclopentadienylgruppen sind; R^1 ein Alkylrest, ein Dialkylsilylen-, Dialkylgermanylen-, Alkylphosphindiyl- oder Alkyliminorest ist, wobei R^1 1 bis 20 Kohlenstoffatome enthält und Cp^1 und Cp^2 verbindet; m 0 oder 1 ist; R^4 ein Alkyl- oder Arylrest ist; M ein Titan-, Zirkonium- oder Hafniumatom ist und [A] ein Anion ist;
wobei die Organoaluminiumverbindung (b) durch die allgemeine Formel (2) wiedergegeben ist:



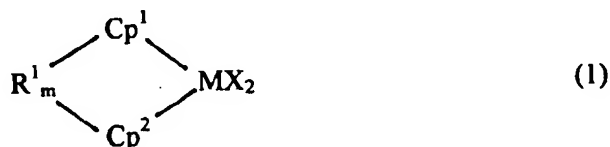
in der jeder der Reste R^2 unabhängig ein Halogen- oder Wasserstoffatom, ein Alkyl-, Alkoxy- oder Arylrest ist und mindestens einer der Reste R^2 ein Alkylrest ist;
wobei das Katalysatorsystem außerdem eine Borverbindung der nachstehenden allgemeinen Formel (4) in einer Menge von 0.01 mol bis 0.8 mol pro mol der Metallocenverbindung (a) enthält:



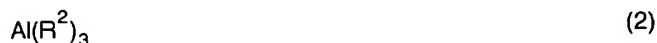
wobei jeder der Reste R^3 unabhängig ein Halogen- oder Wasserstoffatom, ein Alkyl-, Alkoxy- oder Arylrest ist.

5. Verfahren zur Herstellung eines Olefinpolymers nach Anspruch 4, wobei das Katalysatorsystem die Borverbindung in einer Menge von 0.05 mol bis 0.5 mol pro mol der ionischen Metallocenverbindung (a) enthält.
6. Verfahren zur Herstellung eines Olefinpolymers nach Anspruch 4 oder 5, wobei die ionische Metallocenverbindung (a) zu der Borverbindung gegeben wird und das so erhaltene Gemisch mit der Organoaluminiumverbindung und dem Olefin in Kontakt gebracht wird.
7. Verfahren zur Herstellung eines Olefinpolymers nach einem der Ansprüche 1 bis 6, wobei die Borverbindung aus Trifluorboran, Trichlorboran, Tribromboran, Triphenylboran und Tris(pentafluorphenyl)boran ausgewählt wird.

8. Verfahren zur Herstellung eines Olefinpolymers nach einem der Ansprüche 1 bis 7, wobei das Olefin aus Ethylen, Propylen, 1-Buten, 4-Methyl-1-penten, 1-Hexen und 1-Octen ausgewählt wird.
9. Katalysator für die Polymerisation eines Olefins, umfassend eine Metallocenverbindung (A), eine Organoaluminiumverbindung (B) und eine ionische Verbindung (C) als Katalysatorkomponenten, wobei die Metallocenverbindung (A) durch die nachstehende allgemeine Formel (1) wiedergegeben ist:



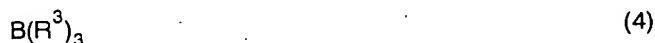
in der Cp¹ und Cp² unabhängig voneinander substituierte oder unsubstituierte Cyclopentadienylgruppen sind; R¹ ein Alkylrest mit 1 bis 20 Kohlenstoffatomen, ein Dialkylsilylen-, Dialkylgermanylen-, Alkylphosphindiy- oder Alkyliminorest ist, der Cp¹ und Cp² verbindet; m 0 oder 1 ist; M ein Titan-, Zirkonium- oder Hafniumatom ist und X ein Fluor-, Chlor-, Brom- oder Iodat, ein Alkyl- oder Arylrest ist; wobei die Organoaluminiumverbindung (B) durch die allgemeine Formel (2) wiedergegeben ist:



in der jeder der Reste R² unabhängig ein Halogen- oder Wasserstoffatom, ein Alkyl-, Alkoxy- oder Arylrest ist und mindestens einer der Reste R² ein Alkylrest ist; wobei die ionische Verbindung (C) durch die nachstehende allgemeine Formel (3) wiedergegeben ist:

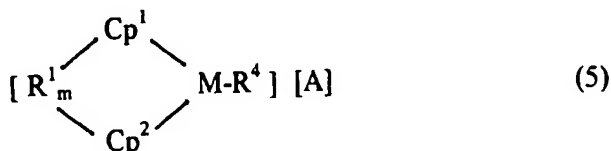


in der [C] ein Kation und [A] ein Anion ist; wobei das Katalysatorsystem außerdem eine Borverbindung (D) der nachstehenden allgemeinen Formel (4) in einer Menge von 0.01 mol bis 0.8 mol pro mol der Metallocenverbindung (A) enthält:



wobei jeder der Reste R³ unabhängig ein Halogen- oder Wasserstoffatom, ein Alkyl-, Alkoxy- oder Arylrest ist.

10. Katalysator für die Polymerisation eines Olefins, umfassend eine ionische Metallocenverbindung (a) und eine Organoaluminiumverbindung (b) als Katalysatorkomponenten, wobei die ionische Metallocenverbindung (a) durch die nachstehende allgemeine Formel (5) wiedergegeben ist:



in der Cp¹ und Cp² unabhängig voneinander substituierte oder unsubstituierte Cyclopentadienylgruppen sind; R¹ ein Alkylrest mit 1 bis 20 Kohlenstoffatomen, ein Dialkylsilylen-, Dialkylgermanylen-, Alkylphosphindiy- oder Alkyliminorest ist, wobei R¹ Cp¹ und Cp² verbindet; m 0 oder 1 ist; R⁴ ein Alkyl- oder Arylrest ist; M ein Titan-, Zirkonium- oder Hafniumatom ist und [A] ein Anion ist; wobei die Organoaluminiumverbindung (b) durch die allgemeine Formel (2) wiedergegeben ist:



in der jeder der Reste R^2 unabhängig ein Halogen- oder Wasserstoffatom, ein Alkyl-, Alkoxy- oder Arylrest ist und mindestens einer der Reste R^2 ein Alkylrest ist;

wobei das Katalysatorsystem außerdem eine Borverbindung der nachstehenden allgemeinen Formel (4) in einer Menge von 0.01 mol bis 0.8 mol pro mol der Metallocenverbindung (a) enthält:

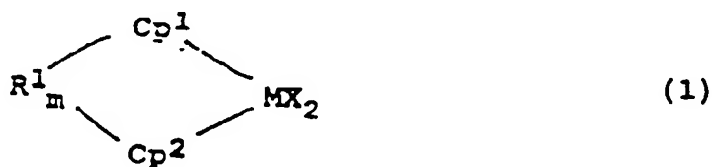


wobei jeder der Reste R^3 unabhängig ein Halogen- oder Wasserstoffatom, ein Alkyl-, Alkoxy- oder Arylrest ist.

Revendications

1. Procédé pour la préparation d'un polymère d'oléfine en utilisant un système de catalyseur de polymérisation qui comprend un composé métallocène (A), un composé organoaluminium (B) et un composé ionique (C) en tant que constituants du catalyseur:

le composé métallocène (A) étant représenté par la formule générale (1) ci-dessous:



dans laquelle Cp^1 et Cp^2 sont indépendamment un groupe cyclopentadiényle substitué ou non-substitué; R^1 est un groupe alkylène ayant 1 à 20 carbones, un groupe dialkylsilylène, un groupe dialkylgermanyène, un groupe alkylphosphindiyle ou un groupe alkylimino qui comporte des liaisons transversales avec Cp^1 et Cp^2 ; m est 0 ou 1; M est le titane, le zirconium ou le hafnium; et X est le fluor, le chlore, le brome, le iode, un groupe alkyle ou un groupe aryle; le composé organoaluminium (B) étant représenté par la formule générale (2):

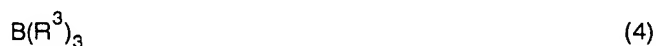


où chacun des groupes R^2 est indépendamment un halogène, un hydrogène, un groupe alkyle, un groupe alkoxy ou un groupe aryle, et au moins l'un des groupes R^2 est un groupe alkyle; et le composé ionique (C) étant représenté par la formule générale (3) ci-après:



où $[\text{C}]$ est un cation et $[\text{A}]$ est un anion;

le système de catalyseur contenant en outre un composé de bore (D) représenté par la formule générale (4) ci-après:

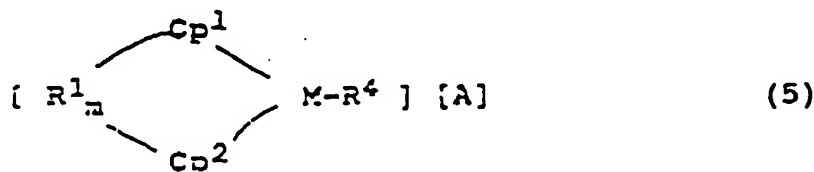


où chacun des groupes R^3 est indépendamment un halogène, un hydrogène, un groupe alkyle, un groupe alkoxy ou un groupe aryle, dans une quantité de 0,01 mole à 0,8 mole par mole du composé métallocène (A).

2. Procédé pour la préparation d'un polymère d'oléfine selon la revendication 1, dans lequel le système de catalyseur contient le composé de bore (D) dans une quantité de 0,05 mol à 0,5 mole par mole du composé métallocène (A).

3. Procédé pour la préparation d'un polymère d'oléfine selon la revendication 1 ou 2, dans lequel le composé métallocène (A) et le composé organoaluminium (B) sont mélangés avec l'oléfine, et le mélange est mis en contact avec le composé ionique (C) contenant le composé de bore (D).

5 4. Procédé pour la préparation d'un polymère d'oléfine en utilisant un système de catalyseur de polymérisation qui comprend un composé métallocène ionique (a) et un composé organoaluminium (b) en tant que constituants du catalyseur: le composé métallocène ionique (a) étant représenté par la formule générale (5) ci-dessous:



15 dans laquelle Cp¹ et Cp² sont indépendamment un groupe cyclopentadiényle substitué ou non-substitué; R¹ est un groupe alkylène, un groupe dialkylsilylène, un groupe dialkylgermanyène, un groupe alkylphosphindiyle ou un groupe alkylimino, R¹ ayant 1 à 20 carbones et comportant des liaisons transversales avec Cp¹ et Cp²; m est 0 ou 1; R⁴ est un groupe alkyle ou un groupe aryle; M est le titane, le zirconium ou le hafnium; et [A] est un anion; et le composé organoaluminium (b) étant représenté par la formule générale (2):



25 où chacun des groupes R² est indépendamment un halogène, un hydrogène, un groupe alkyle, un groupe alcoxy ou un groupe aryle, et au moins l'un des groupes R² est un groupe alkyle; le système de catalyseur contenant en outre un composé de bore représenté par la formule générale (4) ci-après:



30 où chacun des groupes R³ est indépendamment un halogène, un hydrogène, un groupe alkyle, un groupe alcoxy ou un groupe aryle, dans une quantité de 0,01 mole à 0,8 mole par mole du composé métallocène (a).

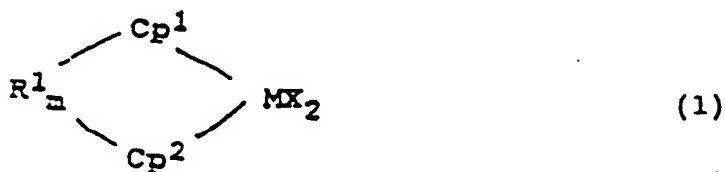
35 5. Procédé pour la préparation d'un polymère d'oléfine selon la revendication 4, dans lequel le système de catalyseur contient le composé de bore dans une quantité de 0,05 mole à 0,5 mole par mole du composé métallocène ionique (A).

40 6. Procédé pour la préparation d'un polymère d'oléfine selon la revendication 4 ou 5, dans lequel le composé métallocène ionique (a) est ajouté au composé de bore, et le mélange résultant est mis en contact avec le composé organoaluminium et l'oléfine.

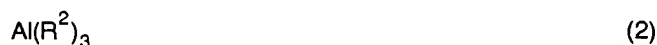
45 7. Procédé pour la préparation d'un polymère d'oléfine selon l'une quelconque des revendications 1 à 6, dans lequel le composé de bore est choisi parmi le trifluoroborane, le trichloroborane, le tribromoborane, le triphénylborane et le tris(pentafluorophényl)borane.

8. Procédé pour la préparation d'un polymère d'oléfine selon l'une quelconque des revendications 1 à 7, dans lequel l'oléfine est choisie parmi l'éthylène, le propylène, le 1-butène, le 4-méthyl-1-pentène, le 1-hexène et le 1-octène.

50 9. Catalyseur pour la polymérisation d'une oléfine, qui comprend un composé métallocène (A), un composé organoaluminium (B) et un composé ionique (C) en tant que constituants du catalyseur: le composé métallocène (A) étant représenté par la formule générale (1) ci-dessous:



dans laquelle Cp^1 et Cp^2 sont indépendamment un groupe cyclopentadiényle substitué ou non-substitué; R^1 est un groupe alkylène ayant 1 à 20 carbones, un groupe dialkylsilylène, un groupe dialkylgermanyène, un groupe alkylphosphindiyle ou un groupe alkylimino qui comporte des liaisons transversales avec Cp^1 et Cp^2 ; m est 0 ou 1; M est le titane, le zirconium ou le hafnium; et X est le fluor, le chlore, le brome, le iode, un groupe alkyle ou un groupe aryle; le composé organoaluminium (B) étant représenté par la formule générale (2):



où chacun des groupes R^2 est indépendamment un halogène, un hydrogène, un groupe alkyle, un groupe alcoxy ou un groupe aryle, et au moins l'un des groupes R^2 est un groupe alkyle; et le composé ionique (C) étant représenté par la formule générale (3) ci-après:



où $[\text{C}]$ est un cation et $[\text{A}]$ est un anion;

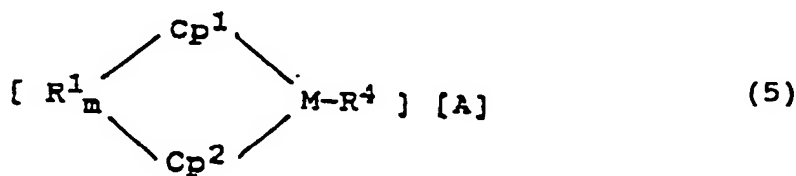
le système de catalyseur contenant en outre un composé de bore (D) représenté par la formule générale (4) ci-après:



où chacun des groupes R^3 est indépendamment un halogène, un hydrogène, un groupe alkyle, un groupe alcoxy ou un groupe aryle, dans une quantité de 0,01 mole à 0,8 mole par mole du composé métallocène (A).

10. Catalyseur pour la polymérisation d'une oléfine qui comprend un composé métallocène ionique (a) et un composé organoaluminium (b) en tant que constituants du catalyseur:

le composé métallocène ionique (a) étant représenté par la formule générale (5) ci-dessous:



dans laquelle Cp^1 et Cp^2 sont indépendamment un groupe cyclopentadiényle substitué ou non-substitué; R^1 est un groupe alkylène ayant 1 à 20 carbones, un groupe dialkylsilylène, un groupe dialkylgermanyène, un groupe alkylphosphindiyle ou un groupe alkylimino, R^1 comportant des liaisons transversales avec Cp^1 et Cp^2 ; m est 0 ou 1; R^4 est un groupe alkyle ou un groupe aryle; M est le titane, le zirconium ou le hafnium; et $[\text{A}]$ est un anion; et le composé organoaluminium (b) étant représenté par la formule générale (2):



où chacun des groupes R^2 est indépendamment un halogène, un hydrogène, un groupe alkyle, un groupe alcoxy ou un groupe aryle, et au moins l'un des groupes R^2 est un groupe alkyle; le système de catalyseur contenant en

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outre un composé de bore représenté par la formule générale (4) ci-après:



où chacun des groupes R^3 est indépendamment un halogène, un hydrogène, un groupe alkyle, un groupe alcoxy ou un groupe aryle, dans une quantité de 0,01 mole à 0,8 mole par mole du composé métallocène (a).

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